

PILOT- AND FULL-SCALE DEMONSTRATION OF ADVANCED MERCURY CONTROL TECHNOLOGIES FOR LIGNITE-FIRED POWER PLANTS

Quarterly Report

(for the period of July 1, 2004 – September 30, 2004)

Prepared for:

AAD Document Control

National Energy Technology Laboratory
PO Box 10940, MS 921-107
Pittsburgh, PA 15236-0940

Cooperative Agreement No. DE-FC26-03NT41897
Performance Monitor: Andrew O’Palko

Prepared by:

Steven A. Benson
Charlene R. Crocker
Kevin C. Galbreath
Jay R. Gunderson
Michael J. Holmes
Jason D. Laumb
Michelle R. Olderbak
John H. Pavlish
Li Yan
Ye Zhuang
Jill M. Zola

Energy & Environmental Research Center
University of North Dakota
Box 9018
Grand Forks, ND 58202-9018

November 2004

DOE DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government, nor any agency thereof, nor any of their employees makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This report is available to the public from the National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Road, Springfield, VA 22161; phone orders accepted at (703) 487-4650.

ACKNOWLEDGMENT

This report was prepared with the support of the U.S. Department of Energy (DOE) National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-03NT41897. However, any opinions, findings, conclusions, or recommendations expressed herein are those of the authors(s) and do not necessarily reflect the views of DOE.

EERC DISCLAIMER

LEGAL NOTICE This research report was prepared by the Energy & Environmental Research Center (EERC), an agency of the University of North Dakota, as an account of work sponsored by DOE. Because of the research nature of the work performed, neither the EERC nor any of its employees makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement or recommendation by the EERC.

PILOT- AND FULL-SCALE DEMONSTRATION OF ADVANCED MERCURY CONTROL TECHNOLOGIES FOR LIGNITE-FIRED POWER PLANTS

ABSTRACT

The overall objective of the project Pilot- and Full-Scale Demonstration of Advanced Mercury Control Technologies for Lignite-Fired Power Plants is to develop advanced innovative Hg control technologies to reduce mercury emissions by 50%–90% in flue gases typically found in North Dakota lignite-fired power plants at costs from one-half to three-quarters of current estimated costs. Power plants firing North Dakota lignite produce flue gases that contain >85% elemental mercury, which is difficult to collect. The specific objectives are focused on determining the feasibility of the following technologies: Hg oxidation for increased Hg capture in wet and dry scrubbers, incorporation of additives and technologies that enhance Hg sorbent effectiveness in electrostatic precipitators (ESPs) and baghouses, use of amended silicates in lignite-derived flue gases for Hg capture, and use of Hg adsorbents within a baghouse. The approach to developing Hg control technologies for North Dakota lignites will involve examining the feasibility of the following technologies: Hg capture upstream of an ESP using sorbent enhancement, Hg oxidation and control using wet and dry scrubbers, enhanced oxidation at a full-scale power plant using tire-derived fuel and oxidizing catalysts, and testing of Hg control technologies in the *Advanced Hybrid*TM filter.

This project was awarded by the U.S. Department of Energy (DOE) National Energy Technology Laboratory (NETL) under Cooperative Agreement No. DE-FC26-03NT41897. The project is cosponsored by the North Dakota Industrial Commission, Minnkota Power Cooperative, Inc., Basin Electric Power Cooperative, Otter Tail Power Company, Great River Energy, Montana–Dakota Utilities Co., BNI Coal Ltd., Westmoreland, and North American Coal Company. Equipment vendors including W.L. Gore & Associates, ADA Technologies Inc., Haldor Topsoe Inc., ALSTOM, and Babcock & Wilcox Company will participate in the program by providing materials and related expertise to test their technologies.

TABLE OF CONTENTS

LIST OF FIGURES	ii
EXECUTIVE SUMMARY	iii
INTRODUCTION	1
WORK PLAN.....	1
BACKGROUND	2
Mercury Control Options	2
Mercury Oxidation	5
EXPERIMENTAL.....	7
Objective and Goals	7
PLANNED SCOPE OF WORK	7
Task 1 – Mercury Control Enhancement for Unscrubbed Systems Equipped with ESPs	7
Task 2 – Mercury Oxidation Upstream of Wet and Dry Scrubbers.....	8
Task 3 – Field Tests to Determine Impacts of Oxidizing Agents on Mercury Speciation ...	8
Task 4 – Particulate and Mercury Control for North Dakota Lignites Using the <i>Advanced Hybrid™</i> Filter Technology	9
Task 5 – Field Testing of Sorbents (revised January 2004).....	9
RESULTS AND DISCUSSION	10
FUTURE WORK – NEXT QUARTER	10
REFERENCES	11

LIST OF FIGURES

1	Pilot-scale ESP and full-scale ESP-FF (TOXECON™) and ESP Hg removal efficiencies as a function of the ACI rate	3
2	Pilot-scale ESP-FF and full-scale ESP-FF (TOXECON™) and ESP Hg removal efficiencies as a function of the ACI rate	4
3	Hg emissions for ACI combined with additives	6
4	Milestone chart.....	10

PILOT- AND FULL-SCALE DEMONSTRATION OF ADVANCED MERCURY CONTROL TECHNOLOGIES FOR LIGNITE-FIRED POWER PLANTS

EXECUTIVE SUMMARY

North Dakota lignite-fired power plants have shown a limited ability to control mercury emissions in currently installed electrostatic precipitators (ESPs), dry scrubbers, and wet scrubbers. This low level of control can be attributed to the high proportions of Hg^0 present in the flue gas. Speciation of Hg in flue gases analyzed as part of the U.S. Environmental Protection Agency (EPA) information collection request (ICR) for Hg data showed that Hg^0 ranged from 56% to 96%, and oxidized mercury ranged from 4% to 44%. The Hg emitted from power plants firing North Dakota lignites ranged from 45% to 91% of the total Hg, with the emitted Hg being greater than 85% elemental. The higher levels of oxidized mercury were only found in a fluidized-bed combustion system. Typically, the form of Hg in the pulverized coal (pc-) and cyclone-fired units was dominated by Hg^0 , at greater than 85%, and the average amount of Hg^0 emitted from North Dakota power plants was 6.7 lb/TBtu.

The overall objective of this Energy & Environmental Research Center (EERC) project is to develop and evaluate advanced and innovative concepts for controlling Hg emissions from North Dakota lignite-fired power plants by 50%–90% at costs of one-half to three-fourths of current estimated costs. The specific objectives are focused on determining the feasibility of the following technologies: Hg oxidation for increased Hg capture in wet and dry scrubbers, incorporation of additives and technologies that enhance Hg sorbent effectiveness in ESPs and baghouses, the use of amended silicates in lignite-derived flue gases for Hg capture, and the use of Hg adsorbents within a baghouse. The scientific approach to solving the problems associated with controlling Hg emissions from lignite-fired power plants involves conducting testing of the following processes and technologies that have shown promise on a bench, pilot, or field scale: 1) activated carbon injection (ACI) upstream of an ESP combined with sorbent enhancement, 2) Hg oxidation and control using wet and dry scrubbers, 3) enhanced oxidation at a full-scale power plant using tire-derived fuel (TDF) and oxidizing catalysts, and 4) testing of Hg control technologies in the *Advanced Hybrid*TM filter insert.

The first pilot-scale tests were started on September 8, 2003, and were completed on September 19, 2003. A 550,000-Btu/hr pc-fired unit, known as the particulate test combustor (PTC), was used to fire lignites and test mercury control options in an unscrubbed system equipped with an ESP and an *Advanced Hybrid*TM filter. Fourteen tests were completed to evaluate various sorbent and mercury oxidant performance on mercury removal across the ESP as functions of feed rate. Ten tests were completed to evaluate various sorbent and mercury oxidant performance on mercury removal across the ESP–*Advanced Hybrid*TM filter configuration as functions of feed rate. Results were reported in the January–March 2004 quarterly report.

Pilot-scale tests using the PTC with a spray dryer (SD)–fabric filter (FF) configuration of Task 2 occurred during a 4-day period, December 8–11, 2003. The effectiveness of three potential Hg sorbents (DARCO[®] flue gas desulfurization [FGD], Amended SilicateTM, and

EERC-treated FGD) and three Hg⁰ oxidation and sorbent enhancement additives (NaCl, CaCl₂, and sorbent enhancement agent [SEA] 2) to enhance the Hg removal efficiency of a SD–FF pollution control system was evaluated using a pilot-scale pc-fired unit. A Center lignite coal was burned in the unit at approximately 580 MJ/hr (550,000 Btu/hr) while Hg concentrations were almost continuously monitored at the SD inlet and FF outlet with continuous mercury monitors to evaluate Hg removal performance. The CMM data were verified with periodic Ontario Hydro (OH) method sampling. The coal and flue gas composition were characterized.

The Hg sorbents and Hg⁰ oxidation and sorbent enhancement additives were evaluated separately, and all except the Amended Silicate™ and EERC-treated FGD were also tested in combination. Nine tests were completed to evaluate the effectiveness of potential Hg sorbents (DARCO® FGD, EERC-treated FGD, and Amended Silicate™) and Hg⁰ oxidation and sorbent enhancement additives (NaCl, SEA 2, and CaCl₂) to remove Hg using a SD and FF. The test matrix is presented in Table ES–1.

Table ES–1. Mercury Control Test Matrix

Coal Additive	Feed Rate, lb/Macf	Sorbent	Injection Rate, lb/Macf
None	NA ^a	None	NA
None	NA	DARCO® FGD	1.84, 3.67, 7.35, and 11.0
None	NA	EERC-treated FGD	1.84, 3.67, and 7.35
None	NA	Amended Silicate™	7.35
NaCl	3.67, 7.35, and 11.0	None	NA
NaCl	3.67, 7.35, and 11.0	DARCO® FGD	3.67
SEA 2	1.84 and 3.67	None	NA
SEA 2	1.84 and 3.67	DARCO® FGD	1.84
CaCl ₂	3.67, 7.35, and 11.0	None	NA
CaCl ₂	3.67, 7.35, and 11.0	DARCO® FGD	3.67

^a Not applicable.

Mercury Sorbent Performance

Baseline results indicate that the SD–FF was ineffective in removing Hg(g). During DARCO® FGD injection, the Hg(g) removal efficiency of the SD–FF greatly improved immediately and continued to improve with increasing injection rates until it approached about 60% at an injection rate of 7.35 lb/Macf. The SD–FF continued to remove Hg(g) after DARCO® FGD injection because of the presence of residual DARCO® FGD on the FF. The EERC-treated FGD provided very good Hg(g) capture, even at a low injection rate of 1.84 lb/Macf. Increasing the injection rate to ≥3.67 lb/Macf slightly improved SD–FF Hg(g) capture. Hg(g) removal efficiencies during the Amended Silicate™ injection averaged 74.9% and were highly variable. The effectiveness of Amended Silicate™ to capture Hg(g) was probably enhanced by the

presence of residual Cl in the system. Both the EERC-treated FGD and Amended Silicate™ sorbents outperformed DARCO® FGD, regardless of the injection rate.

Hg⁰ Oxidation and Sorbent Enhancement Additive Performance

Enhancements were added to the coal prior to introduction to the furnace. HCl concentrations increased significantly with the addition of NaCl to the Center lignite coal; however, Hg(g) concentrations only decreased slightly as the NaCl addition rate increased. Although some residual sorbent remained on the FF from the previous tests, NaCl additions to the Center lignite coal improved SD–FF Hg(total) capture. Negative bias was noted on the CMMs at the SD inlet from the NaCl additions. The results were determined based on the OH method data.

The effect of NaCl additions on Hg(g) and Hg⁰ concentrations are much more pronounced in the presence of DARCO® FGD as compared to the lone addition of NaCl. Apparently, NaCl addition enhances the Hg(g) adsorption capacity of DARCO® FGD. The combination of NaCl addition and DARCO® FGD injection is very effective in capturing Hg(g) in the SD–FF pollution control devices.

Similar to NaCl additions, CaCl₂ additions alone caused Hg(g) and Hg⁰ concentrations to decline gradually with time and increasing CaCl₂ addition rates. The SD–FF Hg(g) removal efficiencies demonstrate that the combination of CaCl₂ addition and DARCO® FGD injection provides much more effective Hg(g) emissions control relative to CaCl₂ addition or DARCO® FGD injection alone. The results are similar to those for NaCl addition because the active component of both compounds that reacts with Hg⁰ to produce Hg²⁺ and/or Hg(p) is the Cl anion.

The SEA 2 additive to the Center lignite greatly improved the Hg(g) removal effectiveness of the SD–FF, especially at the greater addition rate of 3.67 lb/Macf. After SEA 2 addition, the FF outlet Hg(g) concentration gradually increased over about a 30-minute period to its pre-SEA 2 addition concentration. The combination of DARCO® FGD injection at 1.84 lb/Macf and SEA 2 addition provided exceptional SD–FF Hg(g) capture, >90%, even at the lower addition rate of 1.84 lb/Macf. The combination of SEA 2 addition and DARCO® FGD injection provided the best SD–FF Hg(g) removal efficiency, even at the lowest addition and injection rates of 1.84 lb/Macf. NaCl and CaCl₂ addition combined with DARCO® FGD injection provided similar high levels of SD–FF Hg(g) removal, approximately 70%–90%, although the lone addition of SEA 2 at 3.67 lb/Macf also provided a similar level of efficient Hg(g) removal.

A field test to determine impacts of oxidizing agents on mercury speciation took place at Hestkett station at the end of April 2004. Approximately 100 tons of TDF was provided to the Hestkett station by Auburndale Recycling. The TDF was fired at approximately 10% of the total heat input. Mercury emissions were monitored with OH samples at the ESP inlet and the stack. Four OH samples were taken over a period of 2 days to determine the effect TDF has on mercury speciation/removal. Chlorine levels were also measured with and without the TDF. Analysis of

the TDF and Beulah lignite coal fired during the field tests indicated very low moisture and high volatile matter as compared to the coal. The chlorine content of the TDF was much greater at 324 ppm than of the coal at 7.4 ppm, which should affect the mercury speciation in the flue gas. The noteworthy differences in bulk chemistry were the high zinc and iron contents in the TDF versus the high calcium and silica contents of the coal. Preliminary data analyses indicate that the cofired TDF affected mercury partitioning in the gas stream, reducing the fraction of Hg^0 entering the ESP and improving the mercury removal rate.

A flue gas slipstream from Basin Electric Power Cooperative's Leland Olds Station was routed through the trailer-mounted baghouse unit during the April 1 and 2 sorbent injection field tests. As DARCO[®] FGD was injected at various rates at the inlet to the trailer-mounted baghouse, air-to-cloth ratios were varied to achieve face velocities between 6 and 10 ft/min to investigate the effect of face velocity on mercury control.

Papers were presented at two conferences.

PILOT- AND FULL-SCALE DEMONSTRATION OF ADVANCED MERCURY CONTROL TECHNOLOGIES FOR LIGNITE-FIRED POWER PLANTS

INTRODUCTION

North Dakota lignite-fired power plants have shown a limited ability to control mercury emissions in currently installed electrostatic precipitators (ESPs), dry scrubbers, and wet scrubbers (1). This low level of control can be attributed to the high proportions of Hg^0 present in the flue gas. Speciation of Hg in flue gases analyzed as part of the U.S. Environmental Protection Agency (EPA) information collection request (ICR) for Hg data showed that Hg^0 ranged from 56% to 96%, and oxidized mercury ranged from 4% to 44%. The Hg emitted from power plants firing North Dakota lignites ranged from 45% to 91% of the total Hg, with the emitted Hg being greater than 85% elemental. The higher levels of oxidized mercury were only found in a fluidized-bed combustion system. Typically, the form of Hg in the pulverized coal (pc-) and cyclone-fired units was dominated by Hg^0 at greater than 85%, and the average amount of Hg^0 emitted from North Dakota power plants was 6.7 lb/TBtu (1, 2).

The overall objective of this Energy & Environmental Research Center (EERC) project is to develop and evaluate advanced and innovative concepts for controlling Hg emissions from North Dakota lignite-fired power plants by 50%–90% at costs of one-half to three-fourths of current estimated costs. The specific objectives are focused on determining the feasibility of the following technologies: Hg oxidation for increased Hg capture in wet and dry scrubbers, incorporation of additives and technologies that enhance Hg sorbent effectiveness in ESPs and baghouses, the use of amended silicates in lignite-derived flue gases for Hg capture, and the use of Hg adsorbents within a baghouse. The scientific approach to solving the problems associated with controlling Hg emissions from lignite-fired power plants involves conducting testing of the following processes and technologies that have shown promise on a bench, pilot, or field scale: 1) activated carbon injection (ACI) upstream of an ESP combined with sorbent enhancement, 2) Hg oxidation and control using wet and dry scrubbers, 3) enhanced oxidation at a full-scale power plant using tire-derived fuel (TDF) and oxidizing catalysts, and 4) testing of Hg control technologies in the *Advanced Hybrid*TM filter insert.

WORK PLAN

The work plan for this project consists of six tasks outlined as follows:

- Task 1 – Mercury Control Enhancement for Unscrubbed Systems Equipped with ESPs
- Task 2 – Mercury Oxidation Upstream of Wet and Dry Scrubbers
- Task 3 – Field Tests to Determine Impacts of Oxidizing Agents on Mercury Speciation
- Task 4 – Particulate and Mercury Control for North Dakota Lignites Using the *Advanced Hybrid*TM Filter Technology

- Task 5 – Field Testing of Sorbents
- Task 6 – Project Reporting and Management

BACKGROUND

North Dakota lignite-fired power plants have shown a limited ability to control Hg emissions in currently installed ESPs, dry scrubbers, and wet scrubbers (1). This low level of control can be attributed to the high proportion of Hg^0 present in the flue gas. Speciation of Hg in flue gases analyzed as part of the EPA ICR for Hg data showed that Hg^0 ranged from 56% to 96% and the oxidized mercury ranged from 4% to 44%. The Hg emitted from power plants firing North Dakota lignites ranged from 45% to 91% of the total Hg, with the emitted Hg being greater than 85% elemental. The higher levels of oxidized mercury were only found in a fluidized-bed combustion system. Typically, the form of Hg in the pc- and cyclone-fired units was dominated by Hg^0 , at greater than 85%, and the average Hg^0 emitted from North Dakota power plants was 6.7 lb/Btu (1, 2).

The composition of a coal has a major impact on the quantity and form of Hg in the flue gas and, as a result, on the ability of air pollution control devices (APCDs) to remove Hg from flue gas. In general, North Dakota lignitic coals are unique because of a highly variable ash content, ash that is rich in alkali and alkaline-earth elements, high oxygen levels, high moisture levels, and low chlorine content. Experimental results indicate that low-chlorine (<50 ppm) coal combustion flue gases (typical of North Dakota lignite) contain predominantly Hg^0 , which is substantially more difficult to remove than Hg^{2+} (3). The generally high calcium contents of lignite coals may reduce the oxidizing effect of the already-low chlorine content by reactively scavenging chlorine species (Cl , HCl , and Cl_2) from the combustion flue gas. The level of chlorine in flue gases of recently tested North Dakota and Saskatchewan lignites ranged from 2.6 to 3.4 ppmv, respectively, while chlorine contents in the coal on a dry basis ranged from 11 to 18 ppmw, respectively.

Mercury Control Options

The technologies utilized for the control of Hg will ultimately depend upon the EPA-mandated emission limits. Options being investigated have the potential to attain over 90% control of Hg emissions. The Hg control strategies at North Dakota lignite-fired power plants involve, first, the enhancement of existing control technologies and, second, investigation and development of new control technologies. The strategies include sorbent injection with and without enhancements upstream of an ESP or fabric filter (FF) and Hg oxidation upstream of a wet or dry flue gas desulfurization (FGD) system. The new technologies being investigated include Hg capture using the EERC's advanced hybrid particulate collector (AHPC) or the *Advanced Hybrid*TM filter gold-coated materials, baghouse inserts, and carbon beds (4).

Sorbent injection for removing Hg involves adsorption of Hg species by a solid sorbent injected upstream of a particulate control device such as an FF (baghouse) or ESP. Many

potential Hg sorbents have been evaluated (4). These evaluations have demonstrated that the chemical speciation of Hg controls its capture mechanism and ultimate environmental fate.

ACI is the most mature technology available for Hg control. Activated carbons have the potential to effectively sorb Hg^0 and Hg^{2+} but depend upon the carbon characteristics and flue gas composition (4). Most activated carbon research has been performed in fixed-bed reactors that simulate relatively long-residence-time (gas–solid contact times of minutes or hours) Hg capture by an FF filter cake (5–7). However, it is important to investigate short-residence-time (seconds) in-flight capture of Hg^0 because most of the coal-burning boilers in the United States employ cold-side ESPs for controlling particulate matter emissions. The projected annual cost for activated carbon adsorption of Hg in a duct injection system is significant. Carbon-to-mercury weight ratios of 3000:18,000 (lb carbon injected/lb Hg in flue gas) have been estimated to achieve 90% Hg removal from a coal combustion flue gas containing $10 \mu\text{g}/\text{Nm}^3$ of Hg (1). More efficient carbon-based sorbents are required to enable lower carbon-to-mercury weight ratios to be used, thus reducing the costs. Recent testing conducted at the EERC, as shown in Figures 1 and 2, illustrates the effectiveness of sorbents injected upstream of the ESP and baghouse, respectively.

EERC pilot-scale ESP and ESP–FF Hg removal efficiencies for the Fort Union lignite coals from Saskatchewan and North Dakota (Poplar River and Freedom coals) flue gases are compared in Figures 1 and 2 to those obtained at full-scale utility boilers where activated carbons were injected into a bituminous coal combustion flue gas upstream of a compact hybrid particulate collector (TOXECON™ pulse-jet FF) and into bituminous and Powder River Basin

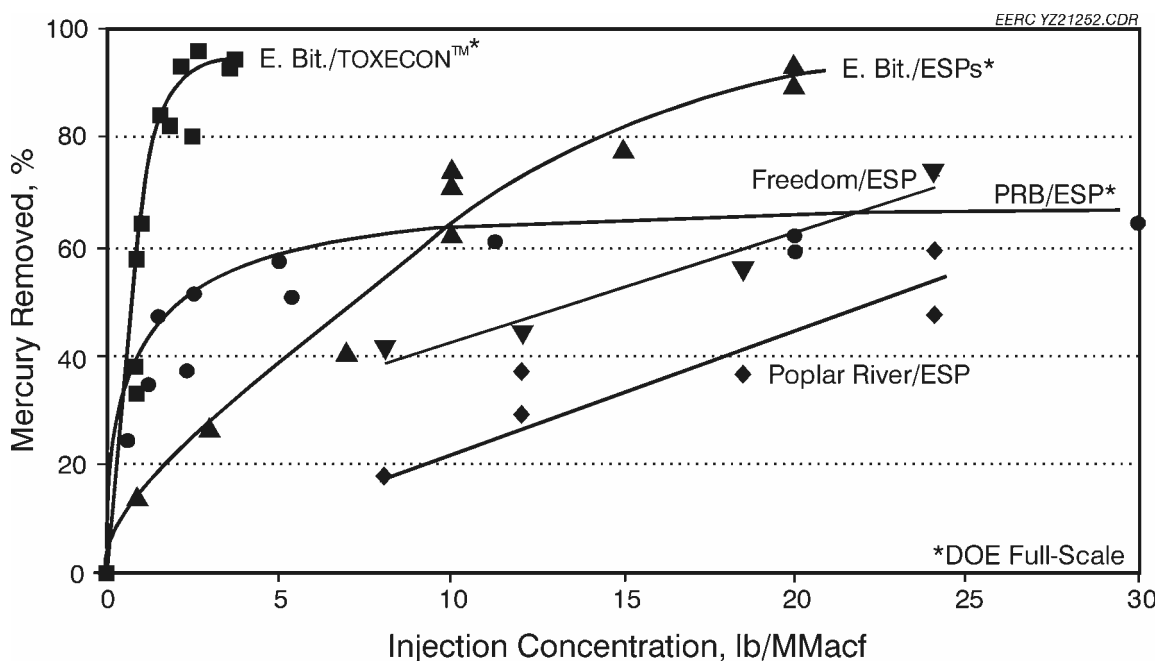


Figure 1. Pilot-scale ESP (1) and full-scale ESP–FF (TOXECON™) and ESP (8) Hg removal efficiencies as a function of the ACI rate.

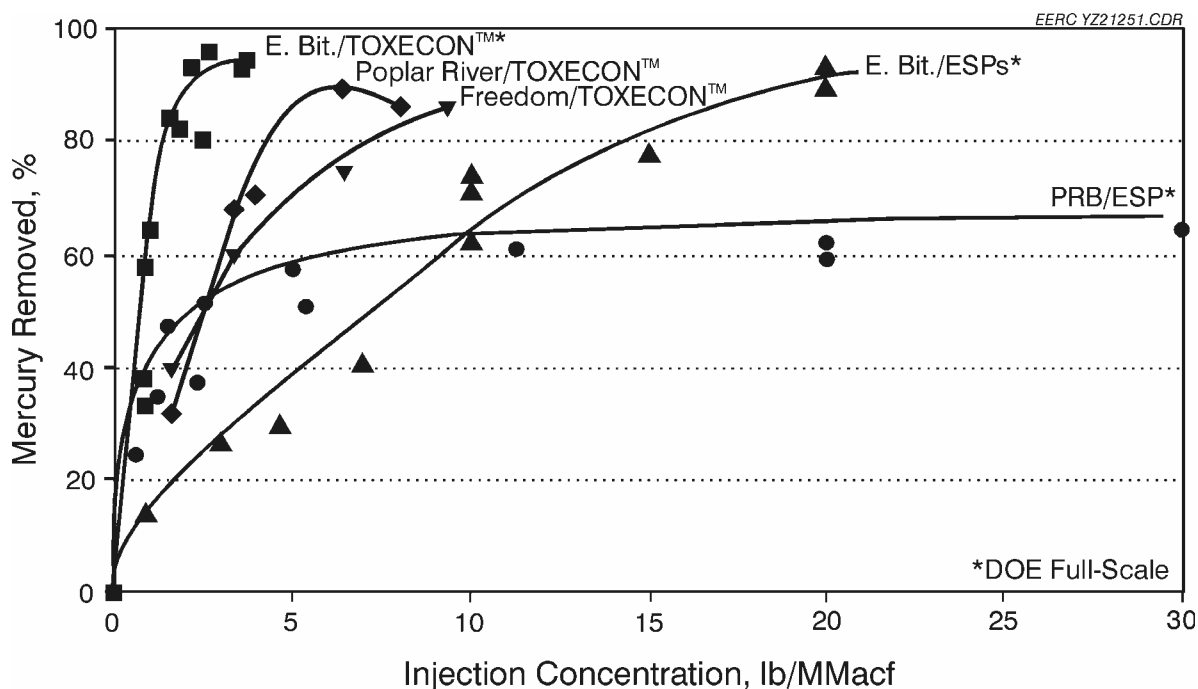


Figure 2. Pilot-scale ESP–FF (1) and full-scale ESP–FF (TOXECON™) and ESP (8) Hg removal efficiencies as a function of the ACI rate.

(PRB) subbituminous coal combustion flue gases upstream of an ESP. Coal type (i.e., composition) is an important parameter that affects the Hg removal efficiency of a control device. During the pilot-scale lignite and utility-scale eastern bituminous coal tests, Hg removal efficiency increased with increasing ACI rates. Conversely, Hg removal efficiency was never greater than 70%, regardless of the ACI rate into the PRB subbituminous coal combustion flue gas. This limitation is probably caused by the low amount of acidic flue gas constituents, such as HCl, that promote Hg-activated carbon reactivity.

Testing conducted at SD baghouse-equipped lignite-fired power plants firing Fort Union lignite indicated poor performance of conventional ACI to control Hg (9). The results indicate control efficiency of less than 35% for DARCO® FGD and lignite-activated carbon (LAC). The poor results are due to the low-acid-gas-containing flue gas and the high proportion of Hg^0 in the flue gas stream. The iodine-impregnated activated carbon (IAC) showed approximately 90% control.

Researchers at the EERC and elsewhere are striving to attain a better understanding of Hg species reactions on activated carbon surfaces in order to produce more efficient sorbents. Functional groups containing inorganic elements such as chlorine or sulfur appear to have a significant role in bonding Hg (10–12). Recently, detailed analysis of sorbents derived from lignites exposed to flue gas and Hg^0 indicated the key species impacting oxidation and retention of Hg on the surface of the carbon contain chlorine and sulfur (13, 14). The chlorine reacts to form organically associated chlorine on the surface, and it appears that the organically associated chlorine on the carbon is the key site responsible for bonding with the Hg^{2+} species.

Amended silicate injection shows promise in controlling Hg emissions at coal-fired power plants (15). The amended silicates have shown improvement factors of 1.5–2 in controlling Hg emissions over activated carbon from subbituminous coal testing in a pilot-scale test. The amended silicates have not been tested using North Dakota lignites.

Mercury Oxidation

Mercury oxidation technologies being investigated for Fort Union lignites include catalysts, chemical agents, and cofiring materials. The catalysts that have been tested include a selective catalytic reduction (SCR) catalyst for NO_x reduction, noble metal-impregnated catalysts, and oxide-impregnated catalysts. The chemical agents include chlorine-containing salts and cofiring fuels that contain oxidizing agents (9).

SCR catalysts were tested for their ability to oxidize Hg; results were mixed. Mercury speciation sampling conducted upstream and downstream of SCR catalysts at power plants that fire bituminous and subbituminous coals (16) showed evidence of mercury oxidation across SCR catalysts when bituminous coals are fired. However, when subbituminous coals are fired, the results indicate limited oxidation. More testing needs to be conducted on low-rank coals. The ability of the SCR system to contribute to oxidation appears to be coal-specific and is related to the chloride, sulfur, and calcium content of the coal, as well as temperature and specific operation of the SCR catalyst including space velocity.

Mercury oxidation catalysts have shown high potential to oxidize Hg⁰. Results in testing a slipstream at a North Dakota power plant indicated over 80% conversion to oxidized mercury for periods of up to 6 months (9). Tests were also conducted using iron oxides and chromium, with little success of oxidation. Galbreath and Zygarlicke (17) have conducted short-term pilot-scale testing with maghemite (γ-Fe₂O₃) additions and were able to transform about 30% of the Hg⁰ in North Dakota lignite combustion flue gases to Hg²⁺ and/or Hg(p) and, with an injection of a small amount of HCl (100 ppmv), nearly all of the Hg⁰ to Hg²⁺. Theoretically, the use of chloride compounds to oxidize Hg⁰ to Hg²⁺ makes sense. The evidence includes chemical kinetic modeling of bench-scale test results, indicating that the introduction of chloride compounds into the high-temperature region of the furnace will most likely result in the production of atomic chlorine and/or molecular chlorine, which are generally thought to be the dominant Hg⁰ reactants in coal combustion flue gases (4).

Fuel additives for mercury oxidation and sorbent enhancement have recently been tested at the EERC. The results of the addition of materials with coal at very low levels along with the ACI upstream of an ESP–FF, *Advanced Hybrid*TM, and ESP-only are illustrated in Figure 3. The first part of the figure shows the baseline data for Hg emissions ranging from 9 to 12 μg/Nm³, with 80%–90% of the Hg in the elemental form. The second case is ACI followed by the addition of Additive 2, showing a reduction in Hg emissions to 90% removal. The third case is the *Advanced Hybrid*TM filter, which produced nearly 90% control efficiency. The final ESP-only case also indicated up to 90% control. The control efficiency for the ESP-only case showed significant potential improvement over past results obtained with the ESP-only illustrated in Figure 1. This technology also has the potential to improve dry FGD baghouse control efficiency.

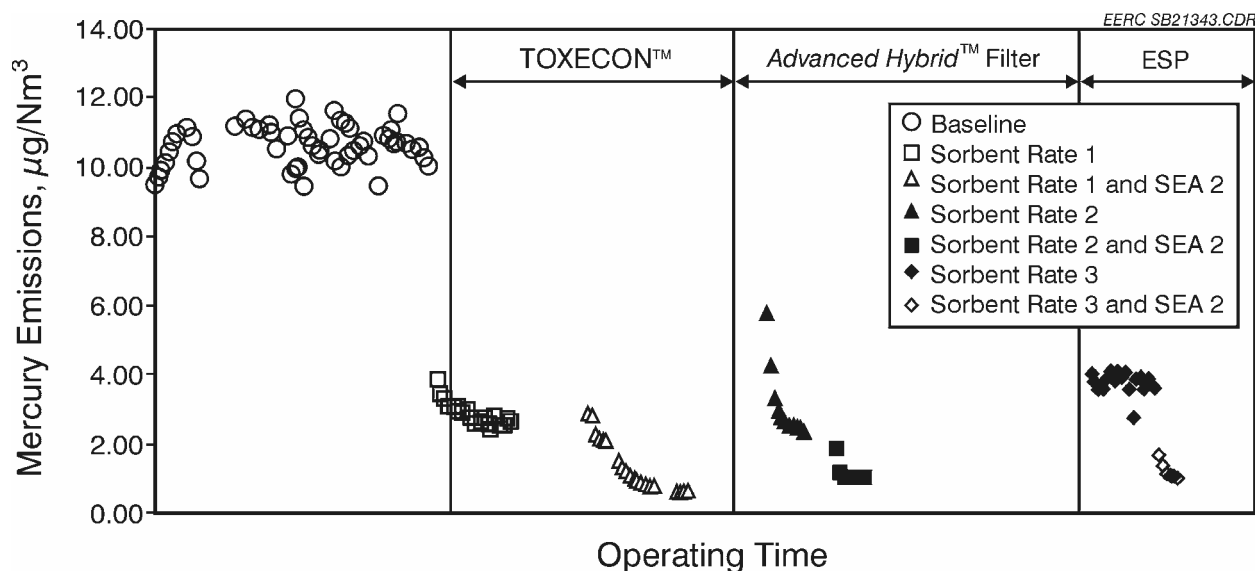


Figure 3. Hg emissions for ACI combined with additives.

Sorbent enhancement technologies (also referred to as additives [SEAs]) have also been investigated by ALSTOM. The sorbent preparation system enhances sorbent performance by changing the physical and chemical nature of the sorbent. The enhancement is expected to be applicable to a significant number of sorbents currently utilized for Hg control. The potential for sorbent enhancement has shown an increase from 68% to over 90% capture of Hg. These tests evaluated the performance of baseline and enhanced sorbents in entrained flow. Sorbents were injected in a duct with synthetic flue gas followed by an ESP.

Cofiring TDF at Otter Tail Power Company's Big Stone Plant has been suspected to contribute to very high reactivity of Hg with fly ash and also with carbon sorbents while a low-chlorine PRB coal is fired (18). During periods of operation that coincide with TDF cofiring, enhanced Hg oxidation and removal of Hg by a particulate control device (PCD) have been observed. When about 3%–5% (Btu basis) TDF was cofired with coal at the power plant, measurements showed that the average PCD inlet Hg speciation was 55% particulate-bound, 38% oxidized, and 6.4% elemental. Without carbon injection to the PCD, the natural Hg capture efficiency of the PCD was 49%. Furthermore, a carbon injection rate of 24 kg carbon/million m^3 flue gas resulted in a 91% total Hg capture efficiency at the PCD. These field test results indicate that cofiring TDF has the effect of changing the speciation of Hg at the inlet to the PCD, which facilitates Hg collection at the PCD.

Since 1995, the U.S. Department of Energy (DOE) has supported development of a new concept in particulate control called the AHPC (18). The AHPC has been licensed to W.L. Gore & Associates, Inc., and is now marketed as the *Advanced Hybrid™* filter by Gore. The *Advanced Hybrid™* combines the best features of ESPs and baghouses in a unique configuration, providing major synergism between the two collection methods, both in the particulate collection step and in the transfer of dust to the hopper. The *Advanced Hybrid™* filter provides ultrahigh collection efficiency, overcoming the problem of excessive fine-particle emissions with

conventional ESPs, and it solves the problem of reentrainment and re-collection of dust in conventional baghouses. The *Advanced Hybrid*[™] filter appears to have unique advantages for Hg control over baghouses or ESPs as an excellent gas–solid contactor. The *Advanced Hybrid*[™] filter technology can be a very cost-effective retrofit technology for plants with existing ESPs.

EXPERIMENTAL

Objective and Goals

The goal of this work is to develop advanced, innovative mercury control technologies to reduce mercury emissions by 50%–90% in flue gases typically found in North Dakota lignite-fired power plants at one-half to three-fourths of current estimated costs. Power plants firing North Dakota lignite produce flue gases that contain >85% elemental mercury, which is difficult to collect. The specific objectives are focused on determining the feasibility of the following technologies: mercury oxidation for increased mercury capture in dry scrubbers and the use of mercury adsorbents within a baghouse.

PLANNED SCOPE OF WORK

Task 1 – Mercury Control Enhancement for Unscrubbed Systems Equipped with ESPs

This task will evaluate and further the ability to control Hg emissions in lignite-fired power systems equipped with an ESP, as well as provide valuable information for enhancing Hg control in other unscrubbed systems. Testing will be performed using sorbent injection on the EERC's particulate test combustor (PTC) equipped with an ESP to evaluate Hg sorbent effectiveness in coal combustion flue gases.

This task will include testing for a full week with up to two North Dakota lignite coals with one activated carbon and ADA Technologies, Inc.'s, Amended Silicate[™]. In addition, a sorbent enhancement technology developed by ALSTOM will be used to enhance a sorbent for injection in the flue gas duct upstream of the ESP. During ACI, several additives and sorbent enhancements will be tested to quantify the improvements in Hg removal with each. The initial testing will involve shorter-term screening tests for evaluation of the SEAs (roughly two a day). A final full-day test will be performed to obtain longer-term results on the performance of a selected additive. This final additive will be selected based on performance during screening tests and with consideration of cost, availability, and any issues associated with use in a utility system. Based on the test results, initial economic evaluations will be performed to determine the cost savings per pound of Hg removal in comparison to the baseline case of ACI without additives.

Task 2 – Mercury Oxidation Upstream of Wet and Dry Scrubbers

Task 2.1 – Elemental Mercury Oxidation Additives

Potential Hg⁰ oxidation additives will be evaluated using the PTC equipped with the refurbished spray dryer absorber (SDA) and AHPC. Pilot-scale testing will involve a North Dakota lignite coal with short-term (1–2-h) screening tests of several oxidation additives including chloride compounds (e.g., sodium chloride, hydrogen chloride, calcium chloride) and potassium iodide, followed by longer-term (8–10-h) evaluations of two or more of the most promising additives. In most cases, the additives will be blended with the coals. Gaseous HCl will be injected into the PTC.

Hg⁰ and total Hg levels will be measured on a nearly continuous basis using a continuous mercury monitor (CMM) at the inlet and outlet locations of the SDA. Slaked lime slurry feed and the SDA product solids will be analyzed for Hg content. Additive blend ratios and injection rates will be varied to evaluate the effectiveness of additives to oxidize Hg⁰. Economic analyses will be performed for the additives that are most effective.

Task 2.2 – Sorbent Injection

NORIT Americas Inc.'s DARCO[®] FGD and lignite-based activated (steam activated at 800°C, [1472°F]) Luscar char (derived from Fort Union lignite) will also be injected upstream of the SDA while a North Dakota lignite is burned in the PTC. One of the sorbents will be pretreated with an EERC proprietary material to enhance its sorption capacity. FGD, activated Luscar char, and the pretreated sorbent will be injected in the absence and presence of the most effective Hg⁰ oxidation additive identified in Task 2.2. In addition, a proprietary sorbent enhancement technology developed by ALSTOM will be tested. CMMs will be used to measure Hg⁰ and total Hg at the inlet and outlet of the SDA during each test. After each test, slaked lime slurry feed and the SDA product solids will be analyzed for Hg and carbon contents.

Task 3 – Field Tests to Determine Impacts of Oxidizing Agents on Mercury Speciation

Task 3.1 – Impacts of Cofiring on Tire-Derived Fuels

The efforts in this subtask involve testing the ability of cofiring TDF with North Dakota lignite to increase the oxidized and particulate forms of mercury at a fluid bed power plant (Montana–Dakota Utilities Heskett Station Unit 2, 85 MW, ESP). Testing will include a baseline run firing 100% lignite at full load and up to 10% TDF (Btu basis). Hg and Cl species levels in the flue gas phase will be measured at the inlet and the outlet of the ESP with and without cofiring the TDF. Coal and TDF will be analyzed for basic proximate, ultimate, sulfur, and ash compositional analysis and Cl, Zn, and Hg. Total Hg collection efficiency of the ESP and the Hg speciation information will be determined.

Task 3.2 – Impacts of Oxidation Catalysts – Coyote Station Slipstream Testing

This task involves testing a Hg oxidation agent. Maghemite combined with very small amounts of HCl has been shown to oxidize Hg^0 in simulated flue gases. Currently, a slipstream reactor to test NO_x reduction catalysts is being installed at Otter Tail Power Company's Coyote Station in North Dakota under an existing EERC project. In Task 3.2, maghemite will be incorporated into a catalyst matrix by Haldor Topsoe, Inc., and placed into the reactor. Small amounts of HCl will be added, and the impact on Hg speciation will be measured across the reactor.

Task 4 – Particulate and Mercury Control for North Dakota Lignites Using the *Advanced Hybrid™* Filter Technology

This task includes reconfiguring the PTC with an ESP followed by the *Advanced Hybrid™* filter system to simulate a full-scale retrofit system. The single-wire tubular ESP will be operated at slightly reduced power to simulate the first one or two ESP fields in a full-scale system, with a goal of removing approximately 90% of the fly ash. Flue gas exiting the ESP with a reduced fly ash level will be routed to the pilot-scale (200-acfm) *Advanced Hybrid™* filter unit.

Two sorbents (activated carbon and silicate-based sorbent) will be injected near the *Advanced Hybrid™* filter inlet. Both continuous and batch injection modes will be tested at a flue gas temperature of 300°F. Specific sorbent injection rates will be determined based on the measured Hg concentration in the flue gas. For continuous injection, the feed rate will be varied from 2500 to 12,000 lb sorbent/lb Hg, and for batch injection the ratio will be set at 6000:1. The sorbent that shows the best performance will be tested at a higher flue gas temperature of 400°F, both in continuous and batch injection modes. CMMs will be used to measure Hg^0 and total Hg vapor at the ESP inlet, the *Advanced Hybrid™* filter inlet, and the *Advanced Hybrid™* filter outlet. Mercury sampling with the Ontario Hydro (OH) method will be conducted to provide Hg species information, dust loading, and particulate collection efficiencies for the retrofit *Advanced Hybrid™* filter unit. EPA Method 26A sampling will be carried out at the *Advanced Hybrid™* filter inlet to determine the chloride level in flue gas entering into the *Advanced Hybrid™* filter unit. Results from the tests will be reduced, compiled, interpreted, and reported. Mercury removal efficiencies for both sorbents will be calculated, compared, and reported across the ESP, the *Advanced Hybrid™* filter, and the ESP–*Advanced Hybrid™* filter.

Task 5 – Field Testing of Sorbents (revised January 2004)

This task will test how effectively Hg can be captured by using a sorbent-based technology in conjunction with a pulse-jet baghouse (PJBH) at a power plant in North Dakota. This task's work plan formerly included evaluation of a Gore technology consisting of a proprietary baghouse insert downstream of the FF that has shown a high potential to control Hg. However, Gore's recent decision to abandon its mercury research program has resulted in elimination of the Gore technology inclusion in the planned scope of work. Additional sorbent evaluations will fill the void. An existing baghouse will be skid-mounted and transported to a power plant in North Dakota and connected in slipstream fashion to allow for testing actual flue gases. Additions to the existing baghouse unit for remote field application will include a control room

for remote operation, piping and flanges for connection to plant ductwork, a variable-speed fan, and a sorbent injection system for Hg control. The PJBH can operate for much longer periods of time than can the pilot-scale AHPC.

The skid-mounted baghouse will be installed downstream of an existing PCD such as an ESP. CMMs will be used to measure Hg⁰ and total Hg vapor at various monitoring ports in the system. Mercury sampling with the OH method will be conducted to provide Hg species information, dust loading, and particulate collection efficiencies. In certain cases, EPA Method 101A may be used to determine the total Hg (only) removed across the baghouse system.

RESULTS AND DISCUSSION

Activities during this quarter involved preparation of the draft final report.

FUTURE WORK – NEXT QUARTER

Work in the upcoming quarter will involve preparation of the draft final report. The report will be completed and submitted to the project sponsors.

The project's milestone chart is presented in Figure 4.

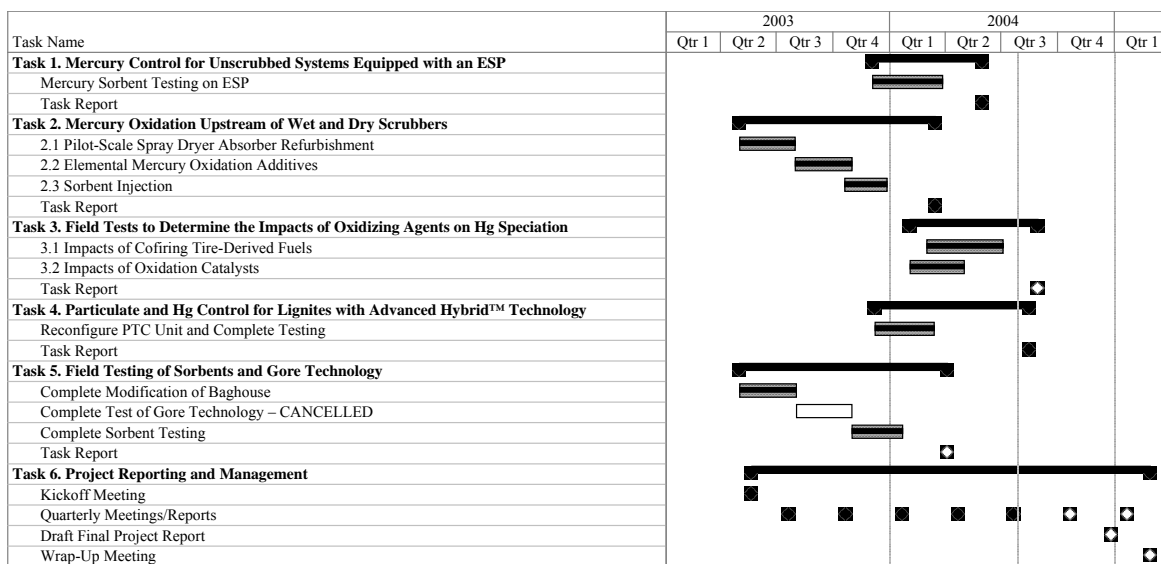


Figure 4. Milestone chart.

REFERENCES

1. Pavlish, J.H.; Holmes, M.J.; Benson, S.B.; Crocker, C.R.; Galbreath, K.C. Application of Sorbents for Mercury Control for Utilities Burning Lignite Coal. *Fuel Process. Technol.* **2004**, *85*, 563–576.
2. Chang, R.; Strohfus, M. *The Evaluation of Chemical Additives for Mercury Emission Control at Great River Energy*; Final Report to the North Dakota Industrial Commission; Jan 2003.
3. Felsvang, K.; Gleiser, R.; Juip, G.; Nielsen, K.K. Activated Carbon Injection in Spray Dryer/ESP/FF for Mercury and Toxics Control. *Fuel Process. Technol.* **1994**, *39*, 417–430.
4. Pavlish, J.H.; Sondreal, E.A.; Mann, M.D.; Olson, E.S.; Galbreath, K.C.; Laudal, D.L.; Benson, S.A. Status Review of Mercury Control Options for Coal-Fired Power Plants. *Fuel Process. Technol.*, **2003**, *82*, (2–3), 89–165.
5. Carey, T.R.; Hargrove, O.W.; Richardson, C.F.; Chang, R.; Meserole, F.B. Factors Affecting Mercury Control in Utility Flue Gas Using Activated Carbon. *J. Air Waste Manage. Assoc.* **1998**, *48*, 1166–1174.
6. Dunham, G.E.; Olson, E.S.; Miller, S.J. Impact of Flue Gas Constituents on Carbon Sorbents. In *Proceedings of the Air Quality II: Mercury, Trace Elements, and Particulate Matter Conference*; McLean, VA, Sept 19–21, 2000; Paper A4-3.
7. Olson, E.S.; Sharma, R.K.; Miller, S.J.; Dunham, G.E. Identification of the Breakthrough Oxidized Mercury Species from Sorbents in Flue Gas. In *Proceedings of the Specialty Conference on Mercury in the Environment*; Minneapolis, MN, Sept 15–17, 1999; pp 121–126.
8. Bustard, J.; Durham, M.; Starns, T.; Lindsey, C.; Martin, C.; Schlager, R.; Bladrey, K. Full-Scale Evaluation of Sorbent Injection for Mercury Control on Coal-Fired Power Plants. In *Proceedings of Air Quality III, Mercury, Trace Elements, and Particulate Matter Conference*; Arlington, VA, Sept 10–12, 2002; Energy & Environmental Research Center: Grand Forks, ND, 2002.
9. Sjostrom, S.; Richardson, C.; Chang, R. *Evaluation of Mercury Emissions and Control Options for Great River Energy*; Final Report for North Dakota Industrial Commission, June 2001.
10. Liu, W.; Vidic, R.D.; Brown, T.D. Optimization of Sulfur Impregnation Protocol for Fixed-Bed Application of Activated Carbon-Based Sorbents for Gas-Phase Mercury Removal. *Environ. Sci. Technol.* **1998**, *32*, 531–538.

11. Ghorishi, S.B.; Kenney, R.M.; Serre, S.D.; Gullett, B.K.; Jozewicz, W.S. Development of a Cl-Impregnated Carbon for Entrained-Flow Capture of Elemental Mercury. *Environ. Sci. Technol.* **2002**, *36*, 4454–4459.
12. Dunham, G.E.; Miller, S.J.; Laudal, D.L. *Investigation of Sorbent Injection for Mercury Control in Coal-Fired Boilers*; Final Report for EPRI and the U.S. Department of Energy; Energy & Environmental Research Center: Grand Forks, ND, Sept 1998.
13. Laumb, J.D.; Benson, S.A.; Olson, E.S. X-Ray Photoelectron Spectroscopy Analysis of Mercury Sorbent Surface Chemistry. *Air Quality III: Mercury, Trace Elements, and Particulate Matter*, Special Issue of *Fuel Process. Technol.* **2004**, *85* (6–7), 577–585.
14. Benson, S.A.; Olson, E.S.; Crocker, C.R.; Pavlish, J.H.; Holmes, M.J. Mercury Sorbent Testing in Simulated Low-Rank Coal Flue Gases. In *Proceedings of the 6th Electric Utilities Environmental Conference*; Jan 27–30, 2003.
15. Lovell, J.; Butz, J.; Broderick, T. Ultimate Fate of Mercury Sorbents. In *Proceedings of the Air Quality III: Mercury, Trace Elements, and Particulate Matter Conference*; Arlington, VA, Sept 9–12, 2002; Energy & Environmental Research Center: Grand Forks, ND, 2002.
16. Laudal, D.L.; Thompson, J.S.; Pavlish, J.H. Brickett, L.A.; Chu, P. Use of Continuous Mercury Monitors at Coal-Fired Utilities. *Air Quality III: Mercury, Trace Elements, and Particulate Matter*, Special Issue of *Fuel Process. Technol.* **2004**, *85* (6–7), 501–511.
17. Galbreath, K.C.; Zygarlicke, C.J.; Mercury Transformations in Coal Combustion Flue Gas. In *Air Quality: Mercury, Trace Elements, and Particulate Matter*, Special Issue of *Fuel Process. Technol.* **2000**, *65–66*, 289–310.
18. Miller, S.J.; Zhuang, Y.; Olderbak, M.R. *Mercury Control with the Advanced Hybrid Particulate Collector*. Technical Progress Report; Energy & Environmental Research Center: Grand Forks, ND, Nov 2002.